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JOHN JAY HOPKINS LABORATORY FOR PURE AND APPLIED SCIENCE

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RADIATION EFFECTS ON SILICON

653 July 65

**First Quarterly Progress Report Covering the Period
June 1 through August 31, 1964**

Work done by:

H. Horiye
H. K. Lintz
D. P. Snowden
V. A. J. van Lint
M. E. Wyatt

Report written by:

D. P. Snowden
V. A. J. van Lint

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I. INTRODUCTION

This first quarterly report on Contract NAS7-289, "Radiation Effects in Silicon," covers the period June 1 through August 31, 1964. During this period work was performed in the following areas.

1. Samples of n-type silicon which had been previously irradiated were studied by electron-spin resonance (ESR) techniques.
2. P-type silicon samples were irradiated and studied by ESR.
3. The technique for measuring lifetime as a function of injection level was refined and applied to a sample of p-type silicon.
4. The temperature dependence of the lifetime was measured in another sample of p-type silicon by a microwave reflectivity technique.

These subjects will now be discussed in more detail.

II. ESR MEASUREMENTS

2.1 INTRODUCTION

The usefulness of spin-resonance measurements to determine the atomic nature of defect structures in solids is well known. Of primary importance has been the orientation dependence of the g value of an electron spin associated with the structure and the hyperfine interaction of that electron with surrounding nuclear spins (both those associated with the host lattice and in some cases with the defect itself). In silicon specifically, resonance measurements have shown an amazing variety of centers produced either directly by irradiation or by irradiation and subsequent annealing -- a much greater number of centers than could ever reasonably be inferred from galvanomagnetic measurements alone. Watkins⁽¹⁾ has recently compiled a list of 28 centers which have been found in silicon irradiated with either electrons or neutrons. In addition inevitably there are other centers which have been observed in other laboratories (including several at General Atomic) which have not yet been reported. With such variety, it is clear that any type of macroscopic measurement cannot possibly reveal the complete picture of the defect structure. In this regard, a warning voiced by Watkins⁽¹⁾ is certainly worth repeating here: "Do not assume that the results (of a macroscopic property study) can be interpreted in terms of a limited number of simple defect structures."

This report will describe the results obtained to date of a study of the types of defects produced by 8 and 30 MeV electrons at fairly high fluxes ($\Phi \gtrsim 10^{17} \text{ cm}^{-2}$) such that the Fermi level is moved a considerable distance from the band edges. Preliminary investigations have been made on both n- and p-type materials.

2.2 EXPERIMENTAL DETAILS

The spin resonance measurements are made at $\sim 9.2 \text{ Gc}$ using a spectrometer employing 60 Mc superheterodyne detection with a balanced crystal mixer. The microwave cavity is constructed of silvered epoxy and oscillates in a rectangular TE_{011} mode with a Q of approximately 2000. Details of the spectrometer and cavity have been presented previously^(2,3) and will not be repeated here. The samples now used are rectangular parallelepipeds ($\sim 1/8 \times 1/8 \times 1/4 \text{ in.}$) oriented with a $[110]$ axis along the long dimension instead of the previously used circular cylinders. This change has been made for ease of sample preparation which outweighs the problems associated with a cavity filling factor which varies slightly with sample orientation.

Measurement temperatures in the ranges 2.0 to 4.2°K and 50 to 70°K are obtained with liquid helium and liquid (or solid) nitrogen at appropriate pressures. In addition, provision has been made to obtain temperatures between 4.2 and 50°K by transferring cold helium gas from a liquid helium storage dewar into the measurement dewar below the cavity and by controlling the cavity temperatures with a small heater around the cavity assembly. This procedure is much more convenient (especially from a safety point of view) than the use of liquid hydrogen coolant and also makes accessible a larger temperature range.

2.3 EXPERIMENTAL RESULTS

The experiments performed to date have been largely exploratory in nature in order to learn over what flux ranges known centers (such as E and J centers) occur at these previously unexplored energies of electron irradiation (8 and 30 MeV) and also to ascertain the general character of the resonance signals from any new centers which might be formed. To this end, we have irradiated both floating-zone and pulled phosphorus-doped silicon with room temperature resistivities between

0.1 and 10 ohm-cm and boron-doped 1 ohm-cm material. Table 1 lists a summary of the various irradiations performed.

In the five pulled samples the only resonance signals seen were due to A centers in concentrations between 3 and $6 \times 10^{15} \text{ cm}^{-3}$. This observation indicates that the Fermi level is still in the vicinity of 0.16 eV below the conduction band for fluxes in the range of several times 10^{17} cm^{-2} at both 8 and 30 MeV (at $\sim 340^\circ\text{K}$) and that considerably higher fluxes would be necessary to investigate possible centers present with the Fermi level near the middle of the gap.

For both the 10 ohm-cm n-type and the 1 ohm-cm p-type samples of irradiations I (30 MeV) and II (8 MeV), resonance centers (in the neighborhood of $g = 2$), if present, were in concentrations of less than about 10^{14} cm^{-3} , which is the limit of sensitivity using the present cavity and sample size. For the 10 ohm-cm n-type samples of irradiation III (whose temperatures were carefully held to 300°K during irradiation by immersing them in flowing water), a small resonance signal was seen at $g = 2.007$ to 2.008 at all three flux levels. The magnitude of these signals was too small, however, to permit orientation-dependent studies. Table 2 lists the approximate concentration of these centers. In the 1 ohm-cm p-type samples small signals are also probably present. All of the above measurements were made at 50°K .

The most fruitful samples by far have been from 0.1 ohm-cm n-type phosphorus-doped, floating-zone material. In the samples irradiated at 8 MeV with $\Phi = 3 \times 10^{17} \text{ cm}^{-2}$, E centers⁽⁴⁾ (an uncharged phosphorus-vacancy complex) have been found with a concentration of $2.5 \times 10^{16} \text{ cm}^{-3}$. This is close to the maximum concentration possible (equal to the total phosphorus concentration $\approx 5 \times 10^{16} \text{ cm}^{-3}$). This center was observed at 50°K in slow passage* using a magnetic field modulation frequency of 100 cps. The center is not seen using a modulation frequency of 1000 cps, and apparently the magnitude of the spin relaxation time, T , is such that the center is in the intermediate region between slow and adiabatic fast passage conditions at this frequency ($T \approx \omega_{\text{mod}}^{-1}$). Also observed in this sample is an isotropic line at $g = 2.0029$ with line width of 0.9 G, with two satellites on each side of the line spaced 1.3 G apart.

*A discussion of passage conditions has been given previously. See Ref. 3.

Table 1
SUMMARY OF SAMPLES IRRADIATED FOR SPIN RESONANCE INVESTIGATIONS*

Irradiation	Irradiation Energy	Temperature of Irradiation	Flux (cm ⁻²)	Sample Description		
				Resistivity (ohm-cm)	Dopant	Type of Growth
I	30 MeV	300°K	0.8×10^{17}	0.09	Phosphorus	Pulled
					Phosphorus	Floating-Zone
					Phosphorus	Floating-Zone
					Boron	Floating-Zone
II	~ 8 MeV	~ 340°K	3×10^{17}	0.4	Phosphorus	Pulled
					Phosphorus	Floating-Zone
					Phosphorus	Floating-Zone
					Boron	Floating-Zone
III	30 MeV	300°K	1×10^{17}	0.1	Phosphorus	Floating-Zone
					Phosphorus	Floating-Zone
					Phosphorus	Floating-Zone
					Boron	Floating-Zone

* Note that for each flux a separate sample of each type is used. For each type, individual resonance samples were cut from adjacent portions of the boule to ensure that they are as nearly similar as possible. For the 8 MeV irradiation the energy is not precisely known and it varied somewhat during the course of the irradiations due to experimental difficulties.

Table 2

APPROXIMATE CONCENTRATIONS OF CENTERS PRODUCING
 RESONANCE SIGNALS AT $g = 2.007$ TO 2.008 IN
 SIM-P-10N4 IRRADIATED AT 300°K WITH 30 MeV ELECTRONS

<u>Flux (cm^{-2})</u>	<u>Concentration (cm^{-3})</u>
1×10^{17}	4×10^{14}
2×10^{17}	3×10^{14}
4.6×10^{17}	1×10^{14}

An E center has not yet been observed in the 0.1 ohm-cm sample irradiated at 8 MeV with a flux of $5 \times 10^{17} \text{ cm}^{-2}$ since we have not yet studied this sample using a 100 cps modulation field. However, because of the large concentration in the sample irradiated with the lower flux, E centers will almost certainly be seen in this sample when the measurement is made.

In the 0.1 ohm-cm samples irradiated at 30 MeV and fluxes of greater than 10^{17} cm^{-2} , resonance signals have also been observed. For the sample irradiated with a flux of $1.4 \times 10^{17} \text{ cm}^{-2}$, a seven-line pattern has been observed with g values ranging from 2.000 to 2.0065. This line pattern has been observed both at 20 and 50°K with field modulation frequencies of both 100 and 1000 cps. The lines are observed in adiabatic fast passage in all cases. The g tensor for this center has not yet been determined from the observed angular dependence of the pattern, but it has been determined that this is not one of the 28 centers tabulated by Watkins⁽¹⁾ by comparison of the observed pattern with similar angular dependent plots made from the data tabulated by him. The signals observed in the samples of irradiation III have not yet been investigated as a function of orientation, so it cannot be said whether these signals correspond to the center described above. The g values, however, cover the same general range.

In the sample irradiated at 30 MeV with a flux of $4.6 \times 10^{17} \text{ cm}^{-2}$, a broad line about 10 G wide* is observed on which the lines described above are superposed. A recorder tracing of this line is shown in Fig. 1. Such a wide line in silicon is surprising since other resonance lines, due both to donors and to defect centers, are typically of the order of 1 G wide, the lines being inhomogeneously broadened by unresolved hyperfine interaction with neighboring Si²⁹ atoms. Note, however, that from the sign of this line (or lines) relative to the g-marker signal we can see that it is traversed under adiabatic fast passage conditions.

*It is of course possible that this is not one line but a series of lines with unresolved splitting. The superposition of the other resonances makes it difficult to assess this possibility.

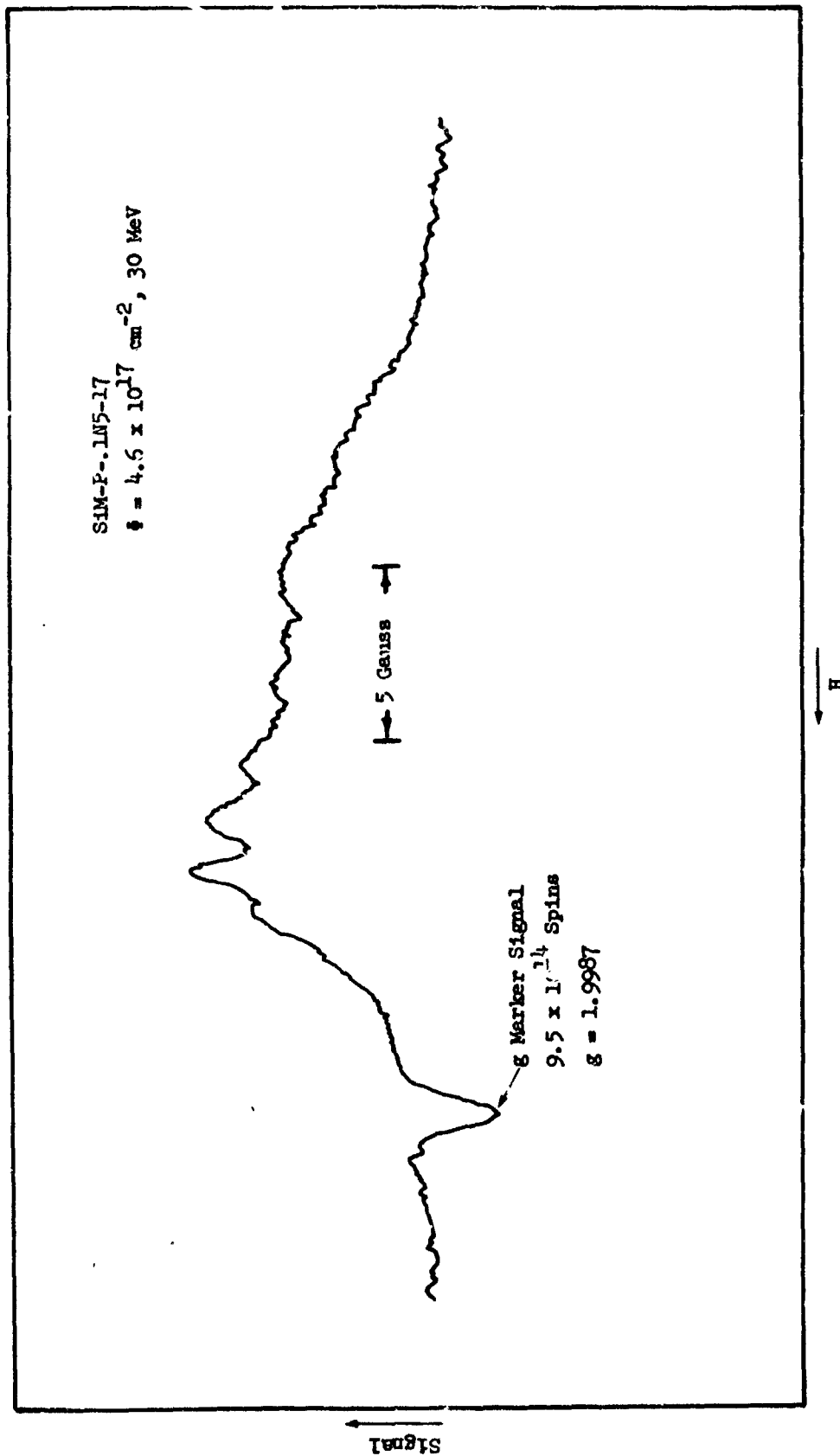


Fig. 1--Resonance signal in SiM-P-.1N5-17 at 50°K

It should also be mentioned that several of these samples also have been studied at 4°K . However, no useful resonance signals have been obtained, even in samples which show good signals at 2 K. Evidently the extremely long spin-relaxation times which occur in silicon at this temperature cause the simple adiabatic fast passage conditions described in Ref. 3 to be violated and one of the more complicated passage cases described by Weger⁽⁵⁾ to prevail. It has not been considered worthwhile, however, to attempt to understand this passage effect, since useful information is more readily obtainable from measurements at higher temperatures.

2.4 DISCUSSION

Although sufficient experimental results at these irradiation energies are not yet available for a complete understanding of the results, several rather random observations can be made.

Although E centers have now been shown to be formed at 8 MeV, they have not been seen in samples irradiated at 30 MeV, both in the experiments reported here and in work we have performed previously on samples irradiated at lower fluxes. It is thus possible to conclude, at least tentatively, that the E center is not the predominant defect formed in floating-zone material irradiated at 30 MeV as it is at lower irradiation energies.

C centers and J centers (the two observable charge states of the divacancy) have not been observed in high resistivity n-type or p-type materials, respectively, whereas they are formed in appreciable concentrations at lower irradiation energies. It must of course be remembered that in the 10 ohm-cm n-type and 1 ohm-cm p-type materials investigated in an attempt to find these centers, the charge carrier concentrations available to populate these centers, which are charged states of the divacancy, are considerably less than available in the 0.1 ohm-cm material which has yielded the several centers described above. However, the sensitivity of our apparatus is adequate to see these centers even if only 10% or 20% of the donor electrons (or acceptor holes) are captured at the appropriate defect. Evidently, at the irradiation energies studied, the divacancy is produced and populated over only a small range of flux. It must of course be remembered that no other centers,

at concentrations greater than a few times 10^{14} cm^{-2} , have been seen in these materials either, so that, although the Fermi level has been moved appreciably towards the center of the gap in these materials, centers observable by ESR techniques (at least under the experimental conditions presently used) are not produced.

2.5 FUTURE PLANS

The work during the next quarter will be concentrated first on measurement of the introduction rates of E centers and also of J centers if a range of fluxes is found which produces them in sufficient concentrations. To assist in studying the production of J centers and other low-concentration centers, the use of a new microwave cavity is planned which will increase the sensitivity of our apparatus by a factor of between 5 and 10. This cavity is quartz filled and operates in the cylindrical TE_{011} mode. The improved sensitivity results from a considerably higher cavity Q and filling factor as compared with the present rectangular cavity. Also to be included when this cavity is installed is provision for optical illumination of the microwave sample at the measurement temperature. Such illumination can change the charge state of a center and make it "visible" by ESR.

In addition, it is planned during the next quarter to begin correlation studies between lifetime and spin resonance measurements, specifically by using the lifetime measurement results as a guide to the energies and fluxes to be used in preparation of samples for ESR studies.

III. LIFETIME STUDIES

3.1 EXPERIMENTAL DETAILS

Lifetime measurements were made utilizing two techniques: the pulsed conductivity technique developed previously⁽³⁾ and a microwave reflectivity technique. The pulsed conductivity technique was improved slightly by utilizing a pulse generator for both the high-injection and low-injection voltage source. In this way, some of the R⁺ noise which was introduced into the system from the dc voltage supply was eliminated.

One of the difficulties with performing lifetime measurements at low temperatures on silicon is the occurrence of rectifying contacts. Such problems are particularly prevalent in p-type silicon in the vicinity of liquid nitrogen temperature. Hence, we have utilized an electrodeless method of measuring the lifetime in silicon which, unfortunately, cannot cover the dynamic range available to the pulsed dc conductivity measurement. The technique was developed under another contract* for use in measuring semiconductor lifetimes down to liquid helium temperatures.

This method involves the measurement of the amplitude and phase shift of an X-band microwave reflected from the sample which is mounted against the shorted end of an X-band waveguide. The microwave circuit is shown in Fig. 2. The microwave power from the klystron is fed to a frequency-measuring cavity and crystal detector and also to a magic T. The magic T splits the power equally between the reference arm and the sample arm and also remixes the reflected signals in a detector crystal. The filter placed in front of the detector crystal is used to reject harmonics of the linear accelerator modulation frequency and accept only the diagnostic X-band frequency. The klystron power supply is stabilized by locking to the resonance frequency of the calibrated adjustable cavity.

The equations for the amplitude and phase of the microwave reflected from the shorted end of the waveguide with the semiconductor sample in front can be solved rigorously and result in a curve of the form shown in Fig. 3. For small injection, the curve can be approximated by a local linear region and the lifetime can be measured directly by observing the exponential decay of the reflected signal amplitude. For high injection, it is necessary to utilize a calibration curve similar to that shown in Fig. 3 to deduce the change in conductivity from the observed signal amplitude.

3.2. EXPERIMENTAL RESULTS

After a number of difficulties were solved, a successful measurement of irradiated p-type silicon by the pulsed dc conductivity method was achieved. The data are now being processed by the semiautomatic film

*Contract No. DA-49-186-AMC-65(X), Harry Diamond Laboratories, U. S. Army Materiel Command, Washington, D. C.

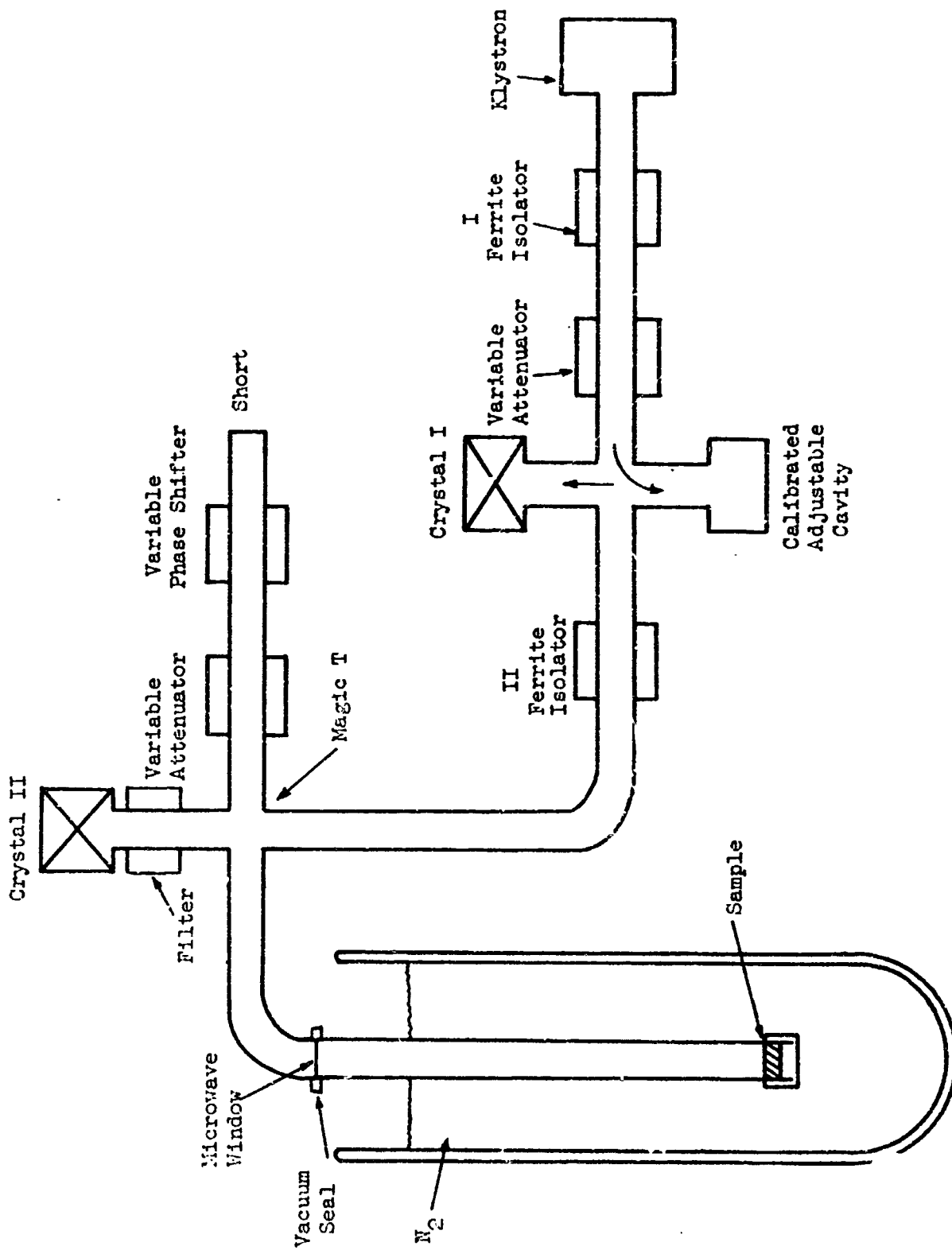


Fig. 2--Microwave circuit

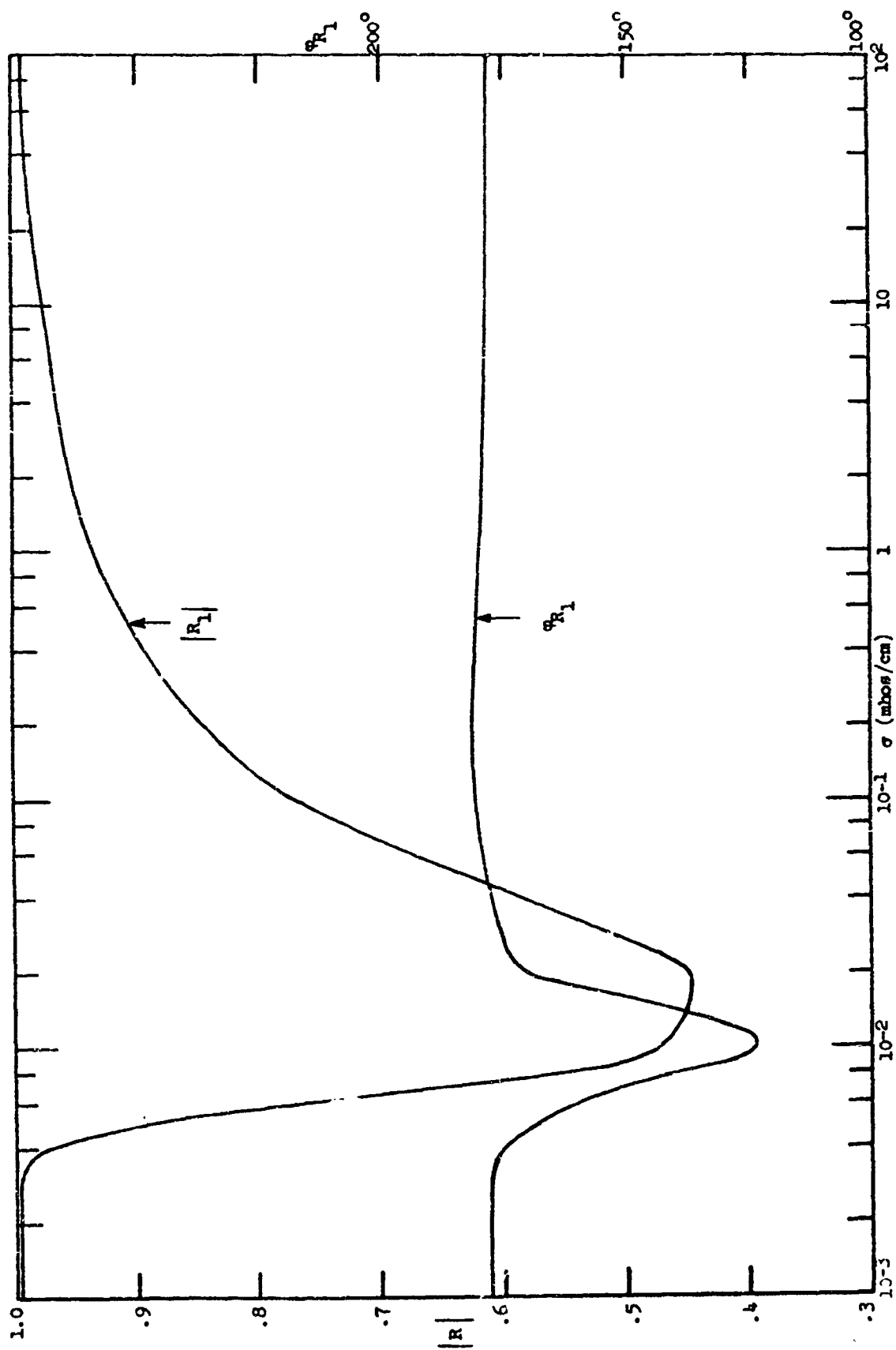


Fig. 3--Amplitude and phase of reflected microwave signal

reader and computer program and will be reported in the next quarterly report.

An experiment was also performed with 10 ohm-cm p-type silicon utilizing the microwave conductivity measurement. These data are also being reduced at present

3.3 FUTURE PLANS

The immediate plans are to complete the data analysis of the two experiments on the p-type silicon: one by the pulsed dc conductivity and the other by the microwave conductivity method. A second experiment by the microwave method on n-type silicon will also be performed to compare with the previous measurements on n-type material.

A theoretical investigation of the temperature dependence of the recombination cross sections in silicon is being performed. This investigation is relying upon the available literature to attempt to determine which cross sections should be temperature dependent and what the functional form of their temperature dependence is likely to be. The purpose of this is to enable us to determine cross sections and activation energies from less than three independent lifetime measurement at each temperature.

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